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Comparative study of some empirical potential functions of diatomic molecules

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Empirical diatomic potential energy function proposed by (i) Morse, (ii) Hulburt-Hirschfelder, (iii) Rydberg, (iv) Linnett, (v) Frost-Musulin, (vi) Varshni, have been studied from the point of their suitability to represent the $A^3\pi(0^+)$ and $X^3\Sigma^-(0^+)$ electronic states of Bi Br molecule. It is concluded that the potential function due to Hulburt-Hirschfelder is more suited in comparison with the others considered in this paper.

1. INTRODUCTION

In the studies of internal structure and interaction of diatomic molecules and in investigation of intensity distribution in molecular band systems, one needs to have a knowledge of potential energy curves which depict the changes in potential energy as a function of internuclear distance.

There are different methods of constructing potential energy curves for the bound states of diatomic molecules. A straight forward method is to solve a Schrodinger equation assuming Born-Ophennheimer approximation to hold good and get the energy eigenvalues. But the procedure is a formidable one and hence there are some simpler alternative methods of constructing potential energy curves like those of Rydberg, Klein and Rees (R-K-R) and Dunham etc. based on experimentally determined molecular parameters. Alternatively empirical functions have been proposed by number of workers wherein there are parameters that are to be adjusted for a given specific molecular state. Some of them are due to Morse (1929), Hulburt-Hirschfelder (1941), Rydberg (1931), Linnett (1940, Frost-Musulin (1954), Varshni (1957), and others.

In the present work we have computed the potential energy curves for the $A\ ^3\pi(0^+)$ and $X\ ^3\Sigma^-(0^+)$ states of Bi Br molecule using different empirical potential energy functions and the results have been compafred with the ones obtained by R-K-R method. A weightage has been given to R-K-R method because it is based on experimentally determined energy values and thence may be taken to be more realistic.

The advantage of choosing Bi Br molecule for the above purpose is that bands arising from high vibrational quanta have been observed and this will help to specifically study the behaviour of empirical potential energy functions at large internuclear distances.

2. Construction of Potential Energy Curves

The experimentally determined energy eigenvalues for different vibrational levels in diatomic molecules can be calculated using experimentally determined constants from the expression

$$E(v) = T_e + w_e(v+\tfrac{1}{2}) - w_e x_e(v+\tfrac{1}{2})^2 + w_e y_e(v+\tfrac{1}{2})^3 + \ldots \quad (1)$$

Rydberg Klein (1932) and Rees (1947) have given an expression to obtain the r_{max} and r_{min} (turning points) for a given vibrational level. The turning points obtained for the two states are entered in Table 1. Spectroscopic constants used in calculations are taken from Herzberg (1950), Lal *et al* (1975).

Table 1. Eigenvalues and turning points of the potential energy curves of $X\ ^3\Sigma^-(0^+)$ (upper values) and $A\ ^3\pi(0^+)$ (lower values) states of Bi Br molecule.

Quantum number	Energy cm^{-1}	R-K-R Turning points	
		r_+ A	r_- A
0	104·55	2·676	2·569
	67·81	2·935	2·804
1	312·96	2·719	2·535
	202·32	2·992	2·763
2	520·42	2·750	2·512
	334·83	3·034	2·738
3	726·96	2·776	2·494
	464·72	3·069	2·719
4	932·55	2·700	2·479
	591·38	3·103	2·703
5	1137·21	2·821	2·466
	714·18	3·130	2·691
6	1340·94	2·841	2·454
	832·51	3·156	2·680
7	1543·72	2·860	2·444
	945·75	3·180	2·671
8	1745·58	2·878	2·434
	1053·27	3·203	2·663
9	1946·49	2·896	2·425
	1154·47	3·224	2·656
10	2146·47	2·913	2·417
	1248·71	3·243	2·650

Spectroscopic constants in cm^{-1}.
$w'_e = 135{\cdot}91$, $w'_e x'_e = 0{\cdot}534$, $w'_e y'_e = -0{\cdot}103$,
$B'_e = 0{\cdot}0428$, $\alpha'_e = 0{\cdot}00025$, $r'_e = 2{\cdot}86696$A,
$w''_e = 209{\cdot}34$, $w''_e x''_e = 0{\cdot}468$, $B''_e = 0{\cdot}0358$,
$\alpha''_e = 0{\cdot}00015$, $r''_e = 2{\cdot}62200$A,
Reduced mass $(u) = 57{\cdot}297 \times 1{\cdot}65972 \times 10^{-24}$ gm.

Potential energies corresponding to the turning points of R-K-R curve are calculated for the following empirical potential energy functions (Steele *et al* 1962). (i) Morse, (ii) Hulburt-Hirschfelder, (iii) Rydberg, (iv) Linnett, (v) Frost-Musulin, and (vi) Varshni.

3. Results and Discussions

The results obtained from the empirical potential functions are shown in Figures 1 and 2. From the study of the graphs the following conclusion can be drawn.

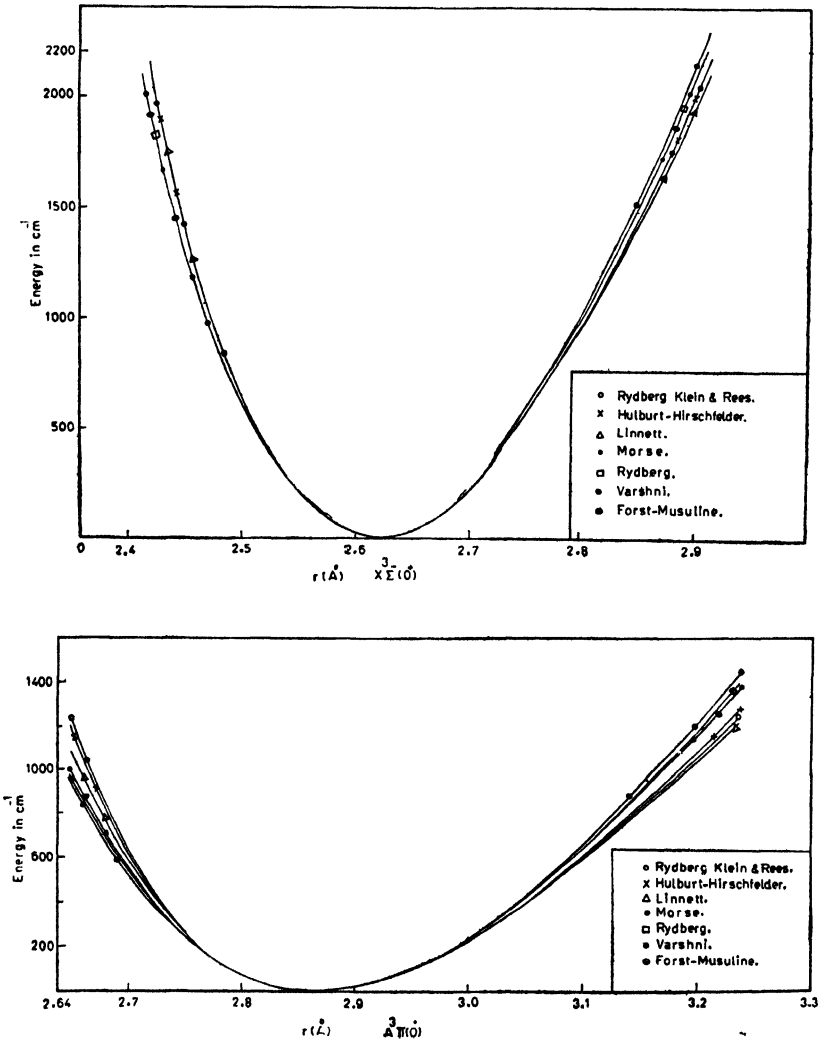

Fig. 2.

The Linnett potential function seems to represent both the electronic states much better in the neighbourhood of equilibrium internuclear distance, and also for r greater than r_e in $A\,^3\pi$ states and r less than r_e in $X\,^3\Sigma^-$ state. But when overall behaviour is considered the Hulburt-Hirschfelder function seems to be the better potential comapared to the rest of the empirical potential functions considered here.

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